

Studies of the Distribution of Menthol in Tobacco,
Filter and Smoke of Menthol Cigarettes.

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6 124-30 (1972)

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1. Introduction

The menthol determination in the tobacco of cigarettes has repeatedly been reported in the literature since 1956. Whereas in the first papers (1,2) the menthol was still determined colorimetrically after reaction with p-dimethylamino benzaldehyde (3), later the authors preferred gas chromatographic methods. Mitchell et al. (4) determined the menthol not only in the tobacco, but also in the smoke of menthol cigarettes and found that practically all the menthol together with the smoke condensate was deposited on the Cambridge filter. Lyerly (5) also analyzed smoke for menthol

Since 1962, in our own laboratory, we have used gas chromatography for the analysis of menthol in tobacco and in filters of menthol-cigarettes, whereby we determined a strongly time-dependent transfer of menthol from the tobacco rope to the cellulose acetate filter. The method developed by us was constantly improved and extended to both trace and smoke analysis. Further, the analysis conditions were so chosen, that in addition to menthol, also menthone as second major constituent of peppermint oil could be quantitative determined.

*Paper given at the 13th Tobacco Colloquium, Brussel, June 1971

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In the following we report the results that we have obtained with this method for the analysis of menthol cigarettes as well as their smoke, whereby the investigation of the effect of the length of storage on the distribution of menthol between tobacco and filter before smoking, or between the main stream of smoke, filter and tobacco butt after smoking, stood in the foreground.

2. Method

2.1 Experimental

The determination of menthol and, if necessary, menthone in tobacco, unsmoked and smoked filters as well as in the smoke of menthol cigarettes and other cigarettes whose flavor contains small amounts of menthol, was carried out by a combination of steam distillation and liquid-liquid ^{partition} distribution through gas chromatography on polypropylene glycol with an FID detector. Benzyl propionate was used as the internal standard (amount = amount of menthol \pm 10%). In Table 1, the experimental conditions for the working up of the material to be analyzed, are summarized. Table 2 gives the gas chromatographic conditions which, as the retention times given show, permit a good separation of menthol, menthone and benzyl propionate from one another and from the solvent. By using two columns in a compensating circuit, even very small amounts of menthol in tobacco (10 ppm) can still be well determined.

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Table 1. Working Up

1. Starting material (an amount corresponding to 10 to 20 cigarettes):
Cigarettes (tobacco + paper) or
not smoked filter with covering or
moisture condensate (EL or CF)* or
smoked filter with covering
2. Addition of 200 ml 0.2N sulfuric acid
3. Steam distillation (60 min.) with simultaneous extraction
with dichloromethane (60 ml/20min. + 60 ml/40 min.) in a
special apparatus
4. Washing of apparatus with 40 ml dichloromethane
5. Drying the extract (about 160 ml) with sodium sulfate
6. Addition of 2 ml n-butanol
7. Concentrate under nitrogen (30°C) to approx. 2 ml
8. Concentrate to gas chromatography

*The precipitation tube is inserted in a special apparatus
and the condensate is dissolved in 10 ml acetone

EL: electrostatic precipitation tube

CF: Cambridge filter

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Table 2. Gas Chromatography

Apparatus:	Perkin-Elmer F 7
Column:	2 m steel, inside diameter 3 mm, 15% Ucon LB 550 X on Supelcoport (80-100 mesh)
Carrier gas:	nitrogen, 30 ml/min.
Temperature:	150°C, isothermal
Detector:	FID
Internal Standard:	benzyl propionate
Retention Time:	menthone 6.2 min (0.51) menthol 9.1 min. (0.75) benzyl propionate 12.2 min. (1.00)

2.2 Reproducibility

Table 3 contains data concerning the reproducibility of the gas chromatography. In so far as peppermint oil is also used for menthol cigarettes as well as pure menthol, this is done generally only for rounding out, so that the menthone concentration is considerably less as the menthol concentration. The concentration ratio of the two substances in our investigations was adjusted accordingly. With higher concentration of menthone the coefficient of variation of menthone is also of the order of 1.5%. The reproducibility of the total method for tobacco, taking into consideration all steps, can be seen from Table 4. For menthol, the coefficient of variation was found to be about 2.5%.

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Table 3. Gas Chromatographic Reproducibility

carried out on solutions of pure substances in n-butanol,
corresponding to the following concentrations in mg/g tobacco:
 I menthol 3.00 + menthone 0.30
 II menthol 1.50 + menthone 0.15

Lösung Substanz in SOLUTION	Menthon	Menthon	Menthon	Menthon
Analysenzahl der Analysen	10	10	10	10
Spannweite RANGE	3,03-3,18	0,27-0,29	1,53-1,59	0,14-0,16
Mittelwert AVERAGE	3,099	0,278	1,552	0,146
Standardabweichung Standard deviation	0,042	0,009	0,021	0,006
Variationskoeffizient(%)V	1,36	3,29	1,36	4,27

Table 4. Reproducibility of the Total Method
for Tobacco

The following were added (in mg/g tobacco) to tobacco con-
taining no additives: menthol 2.00 + menthone 0.20

Substance	Menthon	Menthone
Number of analysis	n 6	6
Range	r 1.90-2.04	0.18-0.19
Average value	\bar{x} 1.969	0.183
Standard deviation	s 0.050	0.007
Coefficient of variation(%)V	2.54	3.78
Recovery (%)	98.4%	91.4

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Table 5. Reproducibility of the Total Method for Smoke.

Cigarette	Age (months)	Menthol content before smoking (in mg/cig.)		
		Rope	Filter	Cigarette
I	3	1.90	0.81	2.71
II	5	1.69	0.93	2.62

Analysis number: for each 5x20 cig. on RM 20/68 EL

Cigarette AFTER SMOKING Geraucht nach dem Rauchen	SMOKE Rauch	Filter	SMOKE II Rauch	Filter
Spannweite RANGE	0.49-0.54	0.77-0.87	0.46-0.51	0.88-0.97
Mittelwert AVERAGE	0.520	0.840	0.480	0.826
Standardabweichung Standard deviation	0.021	0.042	0.019	0.038
Koeffizient der Variation Coefficient of variation	4.1	5.1	3.9	4.8

In the above Table 5, the results of the smoke analysis of two cigarette samples of different age, and therefore different menthol content in the filter, are summarized. The coefficients of variation for the total method including the scattering effect due to the smoking, for the determination of menthol in the smoke and in the filter, are with one exception, of the order of 4%. For these analyses, a smoking machine of the type, RM 20/68 (H. Borgwaldt, Hamburg), with electrostatic precipitator, was used. The smoking was carried out in conformity with the conditions of the CORESTA Standard. The length of the menthol cigarettes in these and in subsequent experiments was 85 mm, that of the cellulose acetate filter, 18 mm. The amount of moist tobacco averaged 895 mg, the burnt dry material, 695 mg.

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Table 6. Recovery of the Total Method for Tobacco

Menthol was dissolved in n-butanol and added to the tobacco in different amounts.

Tabelle 6. Wiedergewinnung (recovery) der Gesamtmethode für Tabak.
Menthol wurde in n-Butanol gelöst und in unterschiedlichen Mengen auf Tabak aufgebracht.

Tabak extrahiert mg/g Extrakt	Menthol aufgebracht mg	Menthol aufgebracht mg/g Tabak MENTHOL ADDED	Menthol gefunden mg/g Tabak		Menthol found MENTHOL FOUND	%
			3,07	3,09		
10	30	3,00	3,11	3,09	102,2 103,0	103,0
10	10	1,00	0,97 1,00	0,99	98,0 100,0	98,5
80	1,5	0,03	0,026 0,026	0,026	85,0 87,0	86,0

2.3 Recovery

In order to check the recovery, menthol was added in three different concentrations and analyzed. As Table 6 shows, the recovery for the whole method is at least 98% if the amount menthol in the menthol cigarettes is of the usual order of magnitude of 1 to 3 mg/cig.. These results agree well with those in Table 4. With very small amounts of menthol (30 ppm), still 86% of the menthol added were recovered.

In order to check the recovery of menthol from the smoke, 2x20 cigarettes each, without menthol, were smoked under the above mentioned conditions. Before the steam distillation, 10 mg of menthol (\approx 0.5 mg/cig.), dissolved in 10 ml acetone, were added to each of the electrostatic precipitator tubes. The yields amounted to 100.7% and 99.8% resp., i.e. they averaged 100.2%.

The completeness of the menthol separation from the smoke by the electrostatic method was checked by connecting a special

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smoke trap filled with glass wool impregnated with triacetate. On the average, 5% of the total smoke menthol was found in this trap. For all basic investigations, the triacetate trap was used in addition. No menthol could be detected in a Cambridge filter which served as a third smoke trap. In addition, a comparison investigation was conducted with the smoking machine CSM 10 (Filtrona, London) and Cambridge filter (diameter 44 mm) (values in mg/cig.)

Rauchmaschine Cigarettenanzahl No. OF CIGARETTES	SMOKING MACHINE			CSM 10/CF			RM 20/68/EL		
	a	b	z	a	b	z			
	5	5	10	20	20	40			
Menthol in der Hauptfalle in MAN TRAP	0.44	0.47	0.46	0.39	0.42	0.41			
Menthol in der Triacetinfalle in TRAP	0.00	0.00	0.00	0.02	0.02	0.02			
Menthol im Rauch IN THE SMOKE	0.44	0.47	0.48	0.41	0.44	0.48			

3. Results

3.1 Transfer of Menthol from Tobacco Roots to the Acetate Filter

Three different methods are used for applying menthol to cigarettes on a production basis. In most cases, menthol solution is sprayed onto the cut tobacco, in a similar way to other flavor solutions. The filters can however also be mentholized directly by dissolving the menthol in the triacetate that is used in the manufacture of cellulose acetate filters. Obviously, both methods can also find combined application. Finally, the aluminum foil that is used for packing the cigarettes can be impregnated with menthol before it is used for packing. The foil gives off the menthol to the cigarettes on storage.

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We have already mentioned that we detected earlier that also the filters of such cigarettes in which only the tobacco was mentholated, very soon contained larger portions of the menthol. In order to follow more exactly the transfer of menthol from the tobacco rods to the acetate filter, we have conducted a series of storage experiments. As can be seen, for example, from Table 7, several per cent of the menthol applied to the tobacco are to be found in the acetate filter, already 8 hours after the cigarettes were manufactured. With menthol cigarettes of the above named type, with 2 to 3 mg/cig. of menthol, about 20% of the menthol go over to the filter in the course of the first month. After two months, this figure has increased already to almost 30%. After 8 months, we found 40% and after 13 months about 44% of the menthol in the filter. This behavior is shown graphically in Fig. 1. The increase in the menthol portion of the filter followed to a limited extent a logarithmic function.

Table 7. Transfer of Menthol into Acetate Filter
During Storage

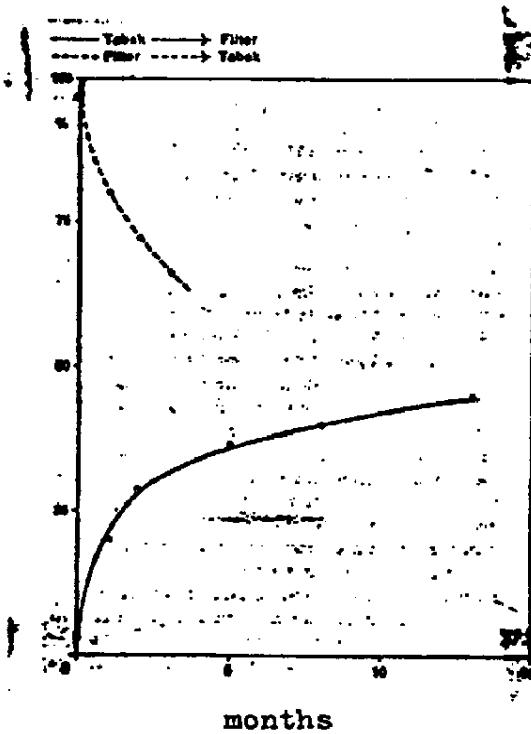
Average values, each of 5 packages of 20 cigarettes

STORAGE TIME Lagerdauer (Monate) (MONTHS)		Mentholf- konzentration mg/g	DISTRIBUTION/ Verteilungskoeffizient Fl/Sv. Filter/Filter	Mentholf mg/Cig.	Mentholf mg/Cig.	Transfer Antrag Filter %
0 (8 hours)	Strong Röhr. Filter	2.00 0.53	0.18	2.74 0.09	2.83	3.2
1	Strong Filter	2.00 3.43	1.49	2.17 0.55	2.72	20.1
2	Strong Filter	1.96 4.06	2.36	1.86 0.73	2.63	28.6
5	Strong Filter	1.75 5.06	3.56	1.55 0.84	2.80	36.2
8	Strong Filter	1.62 6.46	3.80	1.55 1.03	2.66	40.0
13	Strong Filter	1.43 6.46	4.52	1.39 1.03	2.56	43.8

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Figure 1. Percentage of Menthol in the Filter



From Table 7, it can be further seen that in the course of the long storage time under these conditions (room temperature, packaging the cigarette packages additionally in cartons), the decrease in the total menthol of the cigarettes amounted to about 17%. This result is statistically significant. For eliminating the effect of different rope and filter weights, a distribution coefficient was formed from the menthol concentrations in filter and rope. At the end of the investigation, this amounted to about 4.5, and showed thereby that the solubility of menthol in the cellulose acetate is appreciably greater than that in tobacco.

We could show further, that, as expected, that the rate of transfer of menthol from tobacco to the filter is temperature dependent. Whereas the experimental cigarettes after an 8 hour

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storage at about 20°C contained already 3.2% menthol in the filter, the percentage of menthol after the three-fold time at -25°C amounted to only 0.7% (see also Table 9).

3.2 Transfer of Menthol from the Acetate Filter to the Tobacco Röde

The above mentioned results induced us to check whether the menthol could also migrate from the acetate filter to the tobacco röde. In a control experiment, 18 mm acetate filters, each with 1 mg menthol, were therefore glued by hand to 67 mm long röde cigarettes of the same mixture, however without menthol. These cigarettes were stored for several months in tin boxes and samples, taken at monthly intervals, were tested. As the results in Table 8 show, under these conditions there was also a rapid migration of the menthol, however in the opposite direction: after one month, we found about 20% of the menthol in the tobacco röde, after three months about one third of the menthol had transferred to the tobacco. Correspondingly, the distribution coefficient filter/röde for the menthol decreased greatly. Our results do not allow a conclusion to be drawn whether one is dealing here with a true distribution coefficient which depends only on the concentration and not on the absolute amount of menthol.

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Table 8. Menthol Transfer from Acetate Filter to Tobacco During Storage

Average values each of 2x20 cigarettes (0 month 2x10 cigarettes)
The filter was glued by hand to the röde cigarettes, these cigarettes were stored in tin boxes.

STORAGE TIME Lagerdauer (Monate) (MONTHS)		Menthol- konzentration mg/g	DISTRIBUTION KOEFFIZIENT F/FILTER/RÖDE	Menthol mg/Cig.	Menthol mg/Cig.	PERCENTAGE MENTHOL IN FILTER %
0	Strong Röde Filter Filter	0.00 0.23	oo	0.00 1.00	1.00	100.0
1	Strong Filter	0.20 4.72	23.8	0.10 0.76	0.94	80.3
2	Strong Filter	0.27 4.21	15.8	0.26 0.67	0.83	72.4
3	Strong Filter	0.35 4.01	11.5	0.33 0.65	0.66	66.7

The percentage of menthol in the filter as found in this experiment, is also shown in Fig. 1. Here also one is dealing with an approximately logarithmic function. From the extrapolation it follows that for our experimental cigarettes, the menthol equilibrium between tobacco and filter is reached after about a year with a menthol portion of about 45% in the filter, irrespective whether the menthol was originally in the tobacco or the filter. From other investigations, above all with active charcoal, it is known that also other materials contained in tobacco migrate on storage into the filter. This makes the investigation of such cigarettes more difficult, since the results depend on the length of storage. With menthol cigarettes after a short storage time, it is already impossible to decide with certainty which of the three mentioned methods of applying the menthol was used.

3.3 Menthol Content of the Smoke in Relation to the Menthol Distribution in the Cigarette

The menthol distribution is, as has been shown, is very dependent on the method of applying the menthol and on the length of time that the cigarettes have been stored. It is reasonable to assume that this also has a considerable effect on the smoking of the cigarettes, in respect to the distribution of the menthol between the main and the subsidiary smoke flow, as well as the filter and the tobacco butt. We have therefore smoked cigarettes with different amounts of menthol (between 0 and 100%) in the filter. The results of these experiments are summarized in Tables 9 and 10. In the left hand side of Table 9, the results of analyses are given which were obtained on cigarettes before they were smoked; on the right hand side, the results of the smoke analysis. The experimental cigarettes no. 1 to 6 originated from different manufacturing and storage investigations.

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Depending on the total menthol amount and the portion in the filter, about 0.3 to 0.5 mg/cig. menthol were found in the smoke and between 0.6 and 1.2 mg/cig. in the filter. If from this, the menthol retention of the filter is calculated, then for the different experimental cigarettes, this is found to vary between 58 and 73%. A certain trend for increase in retention with increasing percentage of menthol in the filter before smoking, is discernible. For cigarette no. 1, which contains practically all the menthol in the rope, the menthol retention amounts to 63%. This can be considered as the normal retention of the acetate filter, which shows a retention of 46% towards the dry condensate. This signifies that filters of cellulose acetate selectively retain menthol. If the total menthol before smoking is found in the filter, then a part of it is eluted by the smoke out of the filter, so that after smoking, only about 68% remain in the filter.

The menthol contained in the filter before smoking obviously takes part in the menthol equilibrium which exists between smoke and filter. Details of this can be seen in Table 10. By deducting the amount of menthol in the filter before smoking from the total amount of menthol found in the smoke and in the filter (see Table 9), one obtains the amount of menthol entering the filter. After deducting the menthol found in the smoke, this gives the balance in the filter. Depending on the preloading of the filter with menthol, different amounts of the menthol entering the filter are retained or different portions of the menthol already present in the filter are eluted. Obviously this is valid only in the balance, whereas from a molecular point of view, retention and elution always occur concurrently.

One must consequently differentiate between "apparent" retention, which is calculated from the total amount of menthol found in the filter, and the "true" retention, which is obtained

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Table 9. Menthol in the Smoke

Cigarettes from different production lots and storage investigations
 Analysis numbers: for no. 3 and 4, 5x20 cigarettes each (see
 Table 5), otherwise 2x20 cigarettes each

Nr.	TIME Lager- dauer Monate; Monats	BEFORE SMOKING			AFTER SMOKING			APPARENT "SCHLEHENS" Retention %
		Rope Strang mg/Cig.	Filter mg/Cig.	Cigarette mg/Cig.	PERCENTAGE Antritt im Filter %	SMOKE Rauch mg/Cig.	Filter mg/Cig.	
1	0	2.86	0.02	2.88	0.7	0.30	0.67	1.06
2	1	1.85	0.49	2.34	20.9	0.44	0.51	1.05
3	3	1.80	0.61	2.71	29.9	0.52	0.64	1.36
4	5	1.80	0.83	2.62	35.5	0.45	0.53	1.41
5	9	1.71	1.23	2.94	41.8	0.43	1.18	1.61
6	0	0.00	1.00	1.00	100.0	0.29	0.83	0.83

Table 10. Menthol in the Smoke/"True" Retention
 and Transfer to Smoke

Nr.	PERCENTAGE Antritt im Filter %	Menthol Im Strang Rope mg/Cig.	MENTHOL Mentholsgehalt in den Filter mg/Cig.	ENTERING Mentholsgehalt in den Filter %	Filter- ablaßge/ mg/Cig.	TRUE "Wahrer" Retention %**	Mentholsgehalt LEAVING AUS dem Filter (Rauchübergang) mg/Cig.	PERCENTAGE ("GRAVIMETRIC") TO SMOKE
1	0.7	2.86	1.04	36.4	0.65	62.5	0.30	13.6
2	20.9	1.85	0.58	30.3	0.12	21.4	0.44	22.6
3	29.9	1.80	0.55	29.0	0.03	5.5	0.52	37.4
4	35.5	1.80	0.48	28.4	0.00	0.0	0.48	28.4
5	41.8	1.71	0.38	22.2	— 0.05	— 13.2	0.43	32.2
6	100.0	0.00	—	—	— 0.20	—	0.20	—

*Menthol in Rope = 100%

**Menthol entering Filter = 100%

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